PHYSICAL REVIEW A VOLUME 34, NUMBER 4 OCTOBER 1986

Solitary waves in ferroelectric liquid crystals

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(Received 26 August 1985; revised manuscript received 12 May 1986)

The dynamics of bulk molecular reorientation in ferroelectric liquid crystals (FLC's) are modeled by a continuum of elastically coupled, overdamped, massless ferroelectric dipoles under the influence of an external electric field. Numerical solution of this system's equation of motion in one dimension shows that reorientation in response to an applied field step can proceed via the propagation of a solitary wave of universal shape and velocity. Application of the model to an initially helixed configuration shows that solitary waves reorient the bulk only if the applied field is strong enough that its relaxation length is shorter than $\frac{1}{30}$ of the helix pitch. Comparison of our calculations with previous experimental study of the optical response of an FLC indicates that the experimental results cannot be explained by these solitary waves.

I. INTRODUCTION

There is a growing interest in exploring nonlinear behavior of physical systems. The correspondence between experimental observations and the solutions of nonlinear equations of motion has lent support to the concept of solitons and solitary waves as real, useful physical entities. In recent years, the propagation of director waves in nematic and ferroelectric smectic-C^* liquid crystals has been studied as a solitary-wave-type phenomenon. Director orientation couples strongly with polarized light allowing these waves to be observed directly in a light microscope. In 1982, Zhu[1] reported the propagation of director waves in a sheared nematic sample. These results were interpreted by Lin, Shu, and Shen[2] as soliton motion. It was pointed out by Wang[3] that under certain circumstances the motion of the director in these samples could be understood in terms of traveling-wave solutions to nonlinear diffusion equations investigated theoretically by Aronson and Weinberger.[4] That solitary waves might be important in ferroelectric liquid crystals (FLC's) was first suggested by Cladis, Brand, and Finn[5] based on observations of electrically driven reorientation in the smectic-C^* decyloxybenzylidene-p′-amino-2-methylbutylcinnamate (DOBAMBC).[6] In their model the ferroelectric polarization retains the helical configuration intrinsic to the smectic C^* phase, but under an applied electric field the regions of unfavorable polarization become very small. When the applied field is reversed in direction these small regions then have the favored polarization, and they expand by the motion of walls that are identified as sine-Gordon solitons. Other instances of solitary waves in liquid crystals are reviewed by Lin, Shu, and Xu.[7]

In this paper, we report the results of numerical solutions of the equation of motion for elastically coupled, overdamped ferroelectric dipoles under the influence of an external electric field, a model appropriate for director motion in surface-free samples of FLC's. The calculations show that dipoles initially at an orientation of unstable equilibrium in an applied field can be reoriented by the propagation of a solitary wave, with the same asymptotic wave shape and speed resulting from a variety of initial conditions, in excellent agreement with the theory of Aronson and Weinberger.[4] If the region of unstable orientation into which the wave would propagate is infinite in extent, this solitary wave eventually forms and propagates for arbitrarily small applied field. In contrast to this situation, an initially helixed configuration (appropriate for the model of Cladis *et al.*[5]) is reoriented by this wave only for fields above a threshold; below this the reorientation is nonpropagating. We calculate the time required for this reorientation as a function of applied field strength both above and below this threshold. We compare our calculated times with the experimental measurements of Cladis *et al.*[5] and find significant discrepancies that lead us to conclude that this solitary wave does not govern the optical response of helixed FLC's to applied electric field changes.

II. EQUATION OF MOTION

FLC's have their molecules arranged in layers, with the average orientation of the molecular long axes (defining the unit vector $\hat{n}$) tilted an angle ψ_0 from the layer normal (z axis). The ferroelectric polarization **P** is locally normal to both $\hat{n}$ and $\hat{z}$.[8] An electric field **E** applied in the plane of the layers produces a torque $PE\sin\phi$ (where the azimuth ϕ is the angle between **P** and **E**) which can cause easily observed motions of the director on the tilt cone. The configuration of an FLC with the lowest elastic energy has a uniform twist of **P** along the layer normal, i.e., $\phi = qz$, where the pitch p of this helixed configuration defines $q \equiv 2\pi/p$. For a uniformly layered ferroelectric liquid crystal, the free-energy density F is

$$F = \tfrac{1}{2}I\phi_t^2 + \tfrac{1}{2}K(\phi_z - q)^2 - PE\cos\phi\,, \tag{1}$$

where I is the moment-of-inertia density for azimuthal rotations, and K is the elastic constant. We have neglected differences between elastic constants, variations in the tilt angle ψ_0, coupling of the applied field to dielectric anisotropy, flexoelectricity, and the self-field of the ferroelectric polarization; the applicability of these approximations is discussed elsewhere.[9] Variation of Eq. (1) gives the equation of motion, which, with the inclusion of viscosity η that damps azimuthal motion of the director on the tilt cone, is

$$\eta\phi_t = -I\phi_{tt} + K\phi_{zz} - PE\sin\phi\,. \tag{2}$$

In all that follows, we shall neglect inertial torques, since they are smaller than viscous torques for reorientations that are slower than the characteristic time I/η. I is of order $(\frac{1}{12})\rho l^2 \sin^2\psi_0$, where $\rho = 1$ g/cm^3 is the mass density of the liquid crystal and $l = 30$ Å is the molecular length. Measurements of the dynamics of thermal director fluctuations in DOBAMBC indicate $\eta = 0.19\sin^2\psi_0$ g/cm s;[10] the motions we find all will be seen to be *much* slower than the $I/\eta = 4\times 10^{-14}$ s these constants define.

Dividing both sides of the equation of motion (2) by PE, with I set to zero, gives

$$\phi_{t'} = \phi_{z'z'} - \sin\phi\,, \tag{3}$$

where $z' = z/\xi$, $\xi^2 \equiv K/PE$, and $t' = t/\tau$, $\tau \equiv \eta/PE$. This is a nonlinear diffusion equation, of the type investigated in a comprehensive paper by Aronson and Weinberger.[4] They predicted the qualitative behavior of solutions of Eq. (3), and showed that an initial disturbance bounded between two states, one stable and one unstable, whose motion obeys Eq. (3), has as its solution at long times a solitary wave propagating at speed c^* where

$$2\left[\left.\frac{d(\sin\phi)}{d\phi}\right|_{\phi=0}\right]^{1/2} \le c^* \le 2\left[\sup_{\phi\in[0,1]}\left(\frac{\sin\phi}{\phi}\right)\right]^{1/2} \tag{4}$$

(the quantity in the square brackets on the right means "the largest value of $\sin\phi/\phi$ for ϕ in the closed interval from 0 to 1"). Both limits are equal to 2, giving a unique result for c^*.

To be able to observe the evolution of the traveling disturbance in time we transform to a coordinate frame (moving at the wave speed) $z'' = z' - vt'$, and obtain

$$\phi_{t'} = \phi_{z''z''} + v\phi_{z''} - \sin\phi\,. \tag{5}$$

If we choose an initial configuration of ferroelectric dipole orientations such that the asymptotic orientations at very large negative and very large positive z'' are those of stable and unstable equilibrium, respectively, then we expect to see the disturbance evolve into a solitary wave traveling with $v = +2$.

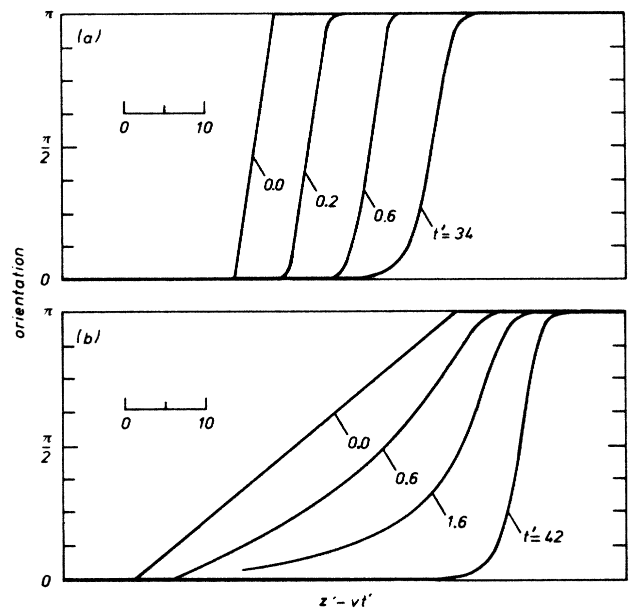

FIG. 1. Wave-shape evolution in an infinite, unhelixed sample. The electric field favors the orientation $\phi = 0$, so dipoles with $\phi = \pi$ are at unstable equilibrium and the wave front moves to the right. (a) Steep initial shape, (b) more gentle shape. The curves are displaced along the abscissa for clarity; the bar shows the scale. The final plot in each sequence shows the same solitary wave traveling at the same speed ($v = 2$).

By comparing solutions obtained using various N, we determined that solving Eq. (5) with $N = 1200$ and $\Delta z'' = 0.05$ would give a solution essentially unaffected by the boundaries and yet not liable to catastrophic collapse at long times.[12]

We observed the evolution of initial states, where ϕ linearly changed from one asymptotic value to the other over a region of varying length, to a solitary wave with constant shape and speed. The final shape was unique and the wave speed asymptotically approached $v = 2$, in excellent agreement with the predicted behavior and demonstrating that the FLC equation of motion (3) does have a solitary-wave solution. Some typical sequences are shown in Fig. 1.

III. NUMERICAL SOLUTION: HELIX-FREE INITIAL STATE

We approximated Eq. (5) using the semi-implicit Crank-Nicolson finite difference scheme.[11] We used N mesh points spaced by $\Delta z''$, with values of ϕ at the two opposite end points fixed. At each time step a set of N simultaneous (but, fortunately, tridiagonal) equations was solved by the Newton-Raphson method. We solved the equation with N in the range 400–1800. This had the effect of solving the problem over different sized domains: Spatial resolution and hence the width of the wave were kept the same, but the boundaries were further removed from the wave front with increasing N. The wave front was constrained to remain in the center of the domain by continual adjustment of the frame velocity v.

IV. NUMERICAL SOLUTION: HELIXED INITIAL STATE

We next considered the evolution of an initial state with ϕ varying with z to model the helixed configuration actually found in bulk samples of FLC's. Although the helix can be unwound by the applied field, the unwinding is a topological process, and requires either reorientation at the boundaries or the introduction of topological defects. We allowed neither of these in the case we considered: In this instance the helix does not unwind, the periodicity of the orientation field remains fixed under applied fields, and the structure of an infinite ferroelectric can be inferred from the structure of one half-period. The boundary conditions then are $\phi(z=0)=0$, and $\phi(z=p/2)=\pi$. To investigate switching behavior induced by an alternating

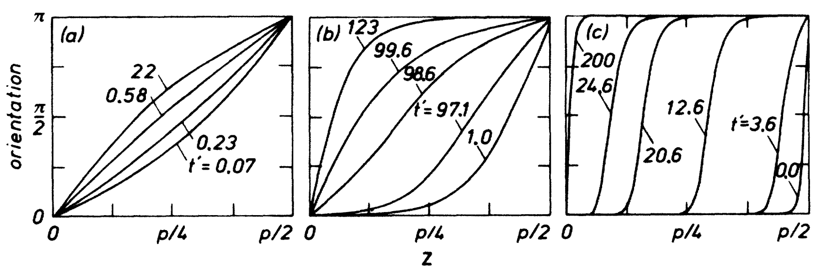

FIG. 2. Dipole reorientation in a helixed sample under the influence of three different electric field strengths: (a) weak field ($E=25$), (b) intermediate field ($E=400$), and (c) strong field ($E=14400$), where E is in units of $K/(p^2P)$. The system is initially in the stable state for a negative applied field. At $t'=0$ a positive field is applied and the dipoles begin to reorient. Each plot shows different stages in the system's evolution towards the final stable state for a positive field.

electric field, we chose as the initial orientation that $\phi(z)$ which satisfies the above boundary condition and which is the configuration of stable equilibrium in a *negative* applied field. This initial orientation was easily calculated since in the steady-state ($\phi_{t'}=0$), Eq. (3) has an exact solution in terms of Jacobian elliptic functions. The evolution of this initial state in various *positive* applied fields is shown in Fig. 2.

For weak applied fields ($p/\xi \ll 1$), the reorientation is small, and is characterized by the time $t_0 \equiv \eta/(Kq^2)$. For larger fields ($p/\xi \lesssim 30$), the reorientation is large and the dynamics depend on applied field strength, with the approach to equilibrium governed by the time constant $\tau=\eta/PE$. At still larger fields ($p/\xi > 30$) the reorientation proceeds by the motion of a wave, whose resemblance to the above found solitary wave increases as the applied field increases. For the purpose of comparison with experiment we "measured" the time required for the midpoint $[\phi(z=p/4)]$ to complete 90% of its reorientation. This time as a function of applied field is shown in Fig. 3.

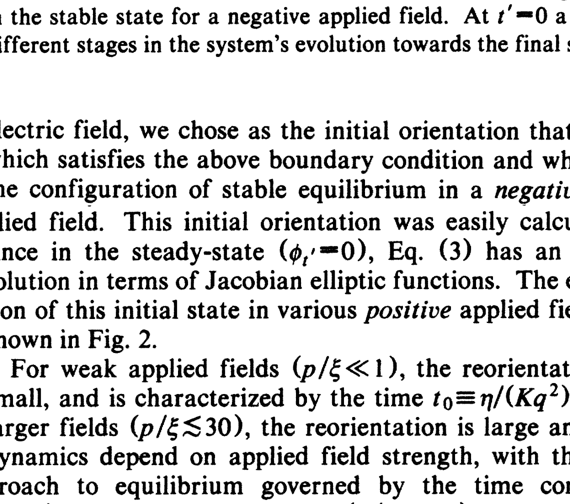

FIG. 3. Optical response time vs electric field. The experimental measurements (▲) are reproduced from Ref. 5. The lower curve (●) shows the results of our computer calculations modeling bulk reorientation. The response time plotted is the time for the midpoint to achieve 90% of its total reorientation. Three characteristic reorientation times are shown for comparison: $t=2.3(2\pi)^{-2}\eta p^2/K$, the field-independent limit for weak fields; $t=2.3\eta/(PE)$ for bulk reorientation with no solitary-wave formation; and $t=(\frac{1}{8})\eta P(PEK)^{-1/2}$ for reorientation achieved by solitary waves alone.

Scaling these times to allow comparison with the measured times of Ref. 5 was accomplished by using the independent measurements on DOBAMBC, with ψ_0 assumed equal to 17°, of $\eta=1.6$ cP, $P=10.8$ statvolt/cm,[10] and $K=1\times10^{-7}$ erg/cm.[13] Further, taking the pitch $p=1.75$ μm (Refs. 14–16) yields $K/(p^2P)=0.11$ V/12 μm and $\eta p^2/K=4.9$ ms.

V. DISCUSSION

It is clear from Fig. 3 that the experimental data cannot be construed as evidence for reorientation by solitary-wave propagation of the kind proposed by Cladis *et al.*[5] and exhibited in the present work by the numerical solutions of a corrected dynamical equation. First, the experimental measurements differ from the calculated times by an order of magnitude. Further, our calculations show the formation of these solitary waves from the helixed initial state only for $p/\xi > 30$, i.e., when $E > 900$ $K/(Pp^2)$. This corresponds, using the previously mentioned scaling parameters, to 100 V applied across a 12 μm thick DOBAMBC specimen. Only three of the experimental measurements fall above the field threshold to be candidates for the modeled solitary-wave reorientation. As mentioned above the calculated and measured times differ by an order of magnitude. More importantly, while the curve of calculated times versus applied field shows a slope on the log-log plot that asymptotically increases to the value of $-\frac{1}{2}$ expected from the solitary-wave velocity being proportional to $E^{1/2}$, the curve connecting the experimental measurements has a slope that decreases with increasing field, and is everywhere less than $-\frac{1}{2}$. On these bases we conclude that the experimental observations of Cladis *et al.*[5] cannot be explained by the proposed solitary-wave switching.

However, we are not surprised by the discrepancies between the calculations and measurements since the calculations are based on a model that neglects several important physical features of FLC switching. First, the model assumes that all the LC director reorientation is one dimensional. In fact, the electric field coherence length ξ can be small compared to the sample thickness, allowing significant orientation changes in the previously ignored direction parallel to the applied field. The observations of

Glogarova, Fousek, Lejcek, and Pavel[17] on thick DOBAMBC specimens show that, at least for slowly varying applied fields, the helix may be completely unwound, and that significant changes in director orientation do occur along the direction parallel to the applied field. Further, our dynamical equation (2) ignores thermal fluctuations. Since $\langle \phi^2 \rangle$ will be of order $kT/(Kl)$, which is of order unity, the calculations, which have assumed that variations in ϕ will be as small as $e^{-p/\xi}$, are unlikely to represent the real reorientation processes in FLC's.

In conclusion, we have shown that a one-dimensional continuum of elastically coupled, overdamped, massless ferroelectric dipoles can be reoriented by an applied electric field by the propagation of a universal solitary wave, in agreement with theories of nonlinear diffusion. This solitary-wave model does not explain previous measurements on applied-field-induced reorientation in ferroelectric liquid crystals.

ACKNOWLEDGMENTS

We thank Professor J. Toomre for his invaluable advice on numerical techniques for the solution of partial differential equations. One of us (M.H.) was supported by grants from the 3M and IBM Corporations. This work was supported by U. S. Army Research Office Grant No. DAAG29-83-K-0076.

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